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Priority documents: DE 100 00 358.3 January 7, 2000
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The following publications were taken into consideration for the determination of patentability:
DE 198 09 095 A1
DE 28 21 804 A1
DE 296 20 553 U1
AT 247,226
US Pat. No. 2,307,270
MANNS, W., LASKOWSKI, Ch.: "Eisen(II)sulfat als Zusatz zur Chromatreduzierung", In the German journal: Beton, vol. 2/1999, pp 78-85.

Title in German of the object of the invention: Verfahren zur Herstellung eines Baustoffs

METHOD FOR THE MANUFACTURING OF A MATERIAL OF CONSTRUCTION

Description

The invention pertains to a method for the manufacturing of a material of construction, which material has a low

chromate-content, and consists of a mixture of cement, in its capacity as binding material, water and filling materials [aggregates], such a sand and gravel.

When concrete or mortar are manufactured on the construction site, the cement, which is acquired to be used as hydraulic binding agent, is mostly processed manually. However, the conventional types of cement, which are used until recently, are considered - due to their chromate content - as allergy triggering agents, responsible for skin eczema, in particular the so-called brickwork scabies.

Chromate-containing cement contains up to 100 ppm of hexavalent chrome compounds (chromates), of which about 20% are soluble. The soluble chromate is the reason for the allergic cement-related eczema. By using cement, having a low chromate content, and cement-containing preparations, having a low chromate content, such as tile adhesives or ready-made mortar, theses diseases can be prevented comprehensively. For this reason, prospective cement-containing materials of construction, which are processed manually, should be made as having an exclusively low chromate content. Cements, having a low chromate content, contain at least less than 2 ppm water-soluble chromate (VI), related to the dry mass.

In this connection, it is known that the chromate content in the cement is reduced by adding a reducing (deoxidizing) agent, namely ferrous sulfate* [*Translator's note: Also known as <$FeSo_4$>; iron

(II) sulfate or iron (2) tetraoxosulfate]. To this end, and in accordance with the German Offenlegungsschrift DE-OS 197 44 035 A1, dry, granular ferrous sulfate [iron (II) sulfate] is added to the cement in an amount of 0.01 to 1 % by weight, when the cement is discharged from a giant silo or storage hopper. When a mortar- or concrete-mixture is being prepared, the granular iron (II) sulfate is dissolved in the mixing water, and - over the course of the mixing - it comes in contact with the chromate (VI)* [*Translator's note: Also known as <$M_2'CrO_4$>, or tetraoxochromate (2-)].

Also, the use of dry, powdery iron (II) sulfate for the reduction of the chromate, is described in Manns, W.; Laskowski, Ch., Ferrous Sulfate as Additive for the Purposes of Reducing the Chromate Content, in the German journal "Beton", vol. 2/1999, pp 78 thru 85, iron(II) sulfate for the reduction of the chromate content is described. The iron (II) sulfates, described therein, should possess a residual content of about 4 moles of crystal water, or less.

In the US pat. No. 2,307, 270, provisions are made that a ready-mixed material of construction is made of a mixture of cement, limestone and iron (II) sulfate. The latter one is immediately dissolved when the material of construction os being mixed.

However, as a result of oxidation with the atmospheric oxygen, iron (II) sulfate loses its effectiveness. For this reason, in the known recommendation, the iron (II) sulfate is

only added to the cement, when the discharge from a giant silo takes place, in order to thus reduce the danger of an undesirable reaction of the admixed granular iron (II) sulfate with the cement.

The cement, which is mixed with the reducing (deoxidizing) agent should be stored properly, in order for a reaction of the iron (II) sulfate to be prevented. Also, certain periods of storage time should not be exceeded because otherwise the reduction agent pronouncedly loses its effectiveness. Basically, the point of departure can be a storage life of about six months.

Moreover, it is disadvantageous that the iron (II) sulfate should be present in granular form. Therefore, a drying up and processing of the same is necessary, which correspondingly results in higher costs of the product.

In professional circles, the use dry bulk cements (silo cements), having of reduced chromate-content [deoxidized chromate] is not considered as necessary at this moment in time because predominantly the cement is mechanically processed, e.g., as ready-mixed concrete.

Taking as point of departure the prior art, the objective to exhibit a method - providing an opportunity for a simple and economically feasible manufacturing of a material of construction, which has a low chromate content - forms the basis of the invention.

The achievement of the set objective consists in the

measures, cited in claim 1. After that for the purposes of manufacturing a material of construction, having a low chrome-content, cement, in its capacity as hydraulic binding agent, filling materials [aggregates], and water are mixed together, and to this mixture there is admixed a mixture of green copperas (vitriol)* [*Translator's note: i.e. <$FeSO_4.7H_2O$>, also known as iron vitriol or iron (II) sulfate heptahydrate, which - in a simplistic way - is just cited as "Grünsalz" ("green salt") in the German text] and an inert material in the form of comminuted limestone or other natural materials, whereby the green copperas is added in an amount of 0.01 % by weight to 3% by weight, related to the amount of cement, while the inert background material is added in an amount between 0.5 and 15% by weight related to the amount of green copperas (vitriol).

The humid green copperas (vitriol) possesses the same reduction properties with regard to the hexavalent chrome compounds as dry iron (II) sulfate in granular form but is having a considerably lower cost. As a result of the addition of the green copperas [iron (II) sulfate) in the amount, in accordance with the invention, an effective reduction [deoxidation] of the chrome content can be achieved to concentrations, which are below the harmful concentrations. In their capacity as background materials, there can be used, e.g., ground limestone, natural minerals or similar fine-grained or powdery substrates, having large surface structure (surface texture). As a result of this,

the handling of the moist green copperas [iron(II) sulfate)] is improved.

Green copperas [iron (II) sulfate precipitates as waste- or subsidiary product in various industrial processes, e.g., from titanium ore, over the course of the manufacturing of titanium dioxide. When titanium dioxide is manufactured in accordance with the sulfate method, the finely comminuted titanium ore is disintegrated with the help of concentrated sulfuric acid. The iron oxide, contained in the ore reacts to iron sulfate, while the titanium ore [rutile] reacts to titanium (IV) sulfate (VI). The separation of the iron sulfate from the titanium (IV) sulfate (VI) takes place as a result of crystallization. Due to the high solubility in water, the iron sulfate crystallizes to green copperas (vitriol) [iron (II) sulfate heptahydrate <$FeSO_4.7H_2O$>, and can be separated. Hence, the green copperas is a waste product of the titanium dioxide manufacturing. Also, green copperas precipitates in acid-pickling [acid-treatment] or etching processes in the metallurgical plants.

In accordance with the invention, the said moist green copperas is used as reduction (deoxidizing) agent when the material of construction, in particular a mortar or concrete mixture, is being mixed. An expensive preparation or drying of the green copperas prior to its use is not required. As a result of this, the costs for a material of construction, having a low chromate content, is reduced several times. Because the green

copperas is added only when mixing takes place, any precautionary measures with regard to the storing property [storage life] of a cement, which go beyond the required extent, do not have to be met.

Due to its large surface structure (surface texture), the inert background material takes care that the water, which is chemically combined in the green copperas, is reduced without a need for a thermal drying process. The said measure contributes to an improved handling over the courses of operation as well as to an improved transportation of the material by trucks to the cement-making plant. As a result of this, the handling with the help of the modified salt of the iron sulfate, i.e. iron (II) sulfate heptahydrate, <$FeSO_4.7H_2O$>, in the cement-making plant as well as the warehousing and the proportioning can be improved. The inert background materials do not exert any influence over the chromate-reduction properties of the green copperas [iron (II) sulfate heptahydrate].

PATENT CLAIMS

Method for the manufacturing of a material of construction, having a low chromate content, whereby cement - in its capacity as hydraulic binding agent, filling materials (aggregates) and water are mixed together, and to latter mixture there is admixed a mixture of green copperas [iron (II) sulfate heptahydrate

<FeSO4.7H2O>] and an inert background material in the form of comminuted limestone or other natural material, so that the green copperas [iron (II) sulfate heptahydrate <FeSO4.7H2O>] is added in an amount of 0.01 % by weight to 3% by weight, related to the amount of cement, and the inert background material is added in an amount between 5% by weight and 15% by weight, related to the amount of green copperas [iron (II) sulfate heptahydrate <FeSO4.7H2O>].

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